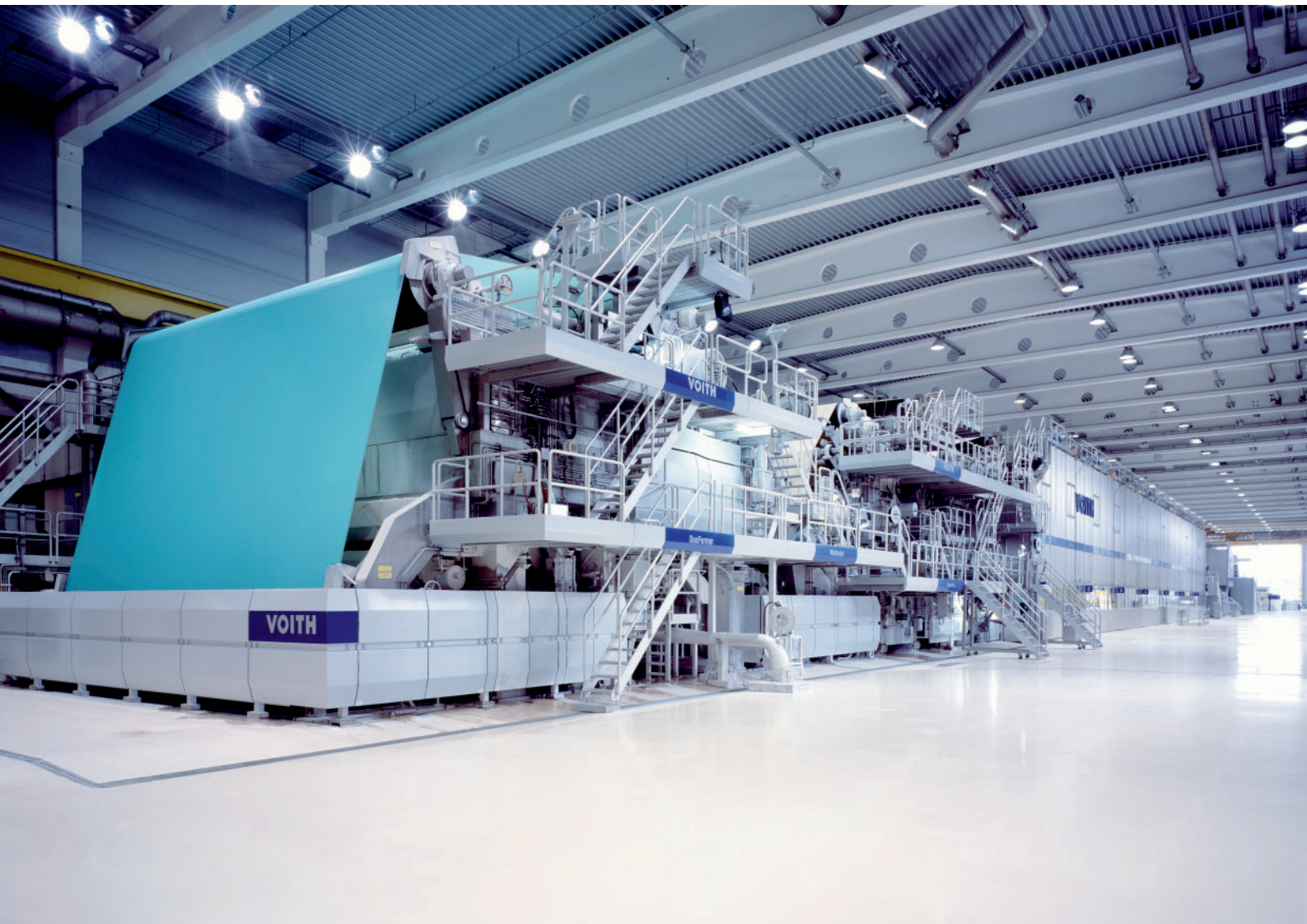




Speed up your success – with gas applications. Innovative solutions in papermaking.

Linde Gas

*Linde*



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## Innovative partners. Linde Gas and the pulp and paper industry.

As one of the leading industrial gas suppliers in the world, Linde Gas is dedicated to meeting the needs of the pulp and paper industry. Every mill and every single process calls for special consideration, so that practical and profitable tailor-made applications can be developed on the basis of our valuable experience and specialist know-how. Our active research and development work enables us to convert new ideas into new technologies that help our customers.

Linde Gas has a wealth of knowledge and experience concerning the use of gas-related technologies in the pulp and paper industry. Linde Gas has particularly developed a wide range of carbon dioxide applications for pulp and papermaking processes. We have also contributed to the development of various bleaching processes, including oxygen delignification and ozone bleaching. Our experts work closely together with customers in production, research, and development, in order to achieve practical solutions that improve the overall mill economy and also reduce environmental impacts.

### **Gas applications in pulp and papermaking processes**

Gases like carbon dioxide (CO<sub>2</sub>) and oxygen (O<sub>2</sub>) can be used in many ways to improve industrial processes. Carbon dioxide is nowadays widely used in the pulp and paper industry. The addition of CO<sub>2</sub> in pulp washing, for instance, is a well-established, patented technology, used in more than 30 fiber lines around the world – including both unbleached and bleached fiber lines.

CO<sub>2</sub> can be used in paper machines to adjust and stabilize pH, to buffer the papermaking system, to reduce calcium levels, or to increase dewatering, for instance. Linde Gas has installations at various positions between the start of the stock preparation and the headbox in around 40 paper machines, running with chemical pulps, mechanical pulps and recycled material.

# Advanced solutions for optimized processes. CO<sub>2</sub>-based technologies in papermaking.

## **ADALKA® Process Stabilizer**

ADALKA® is a patented process where a buffering solution, formed by a combination of CO<sub>2</sub> and caustic soda (NaOH), is added to the stock preparation to regulate and stabilize pH, alkalinity, and calcium levels in the papermaking process. The bicarbonate/carbonate solution, formed through the mixing of CO<sub>2</sub> and NaOH, is produced on site, in a Linde Gas ACU™ alkalinity control unit. Alkalinity and pH can be adjusted independently according to the process requirements.

## **GRAFICO® Calcium Carbonate Saver**

GRAFICO® is a patented application designed to reduce the dissolution of calcium carbonate filler in neutral processes using mechanical pulp and/or de-inked pulp (DIP). Adding carbon dioxide or bicarbonate to the papermaking process can cut calcium levels in the papermaking system by over 50%. Conditions in paper machines are often such that CaCO<sub>3</sub> starts to dissolve, which can lead to problems with runnability, precipitation, deposits and higher consumption of many chemicals.

## **CODIP® Process Improver**

The patented application CODIP® has been developed primarily for newsprint production, where de-inked pulp is used as a raw material. Carbon dioxide is added to the papermaking process, producing benefits including lower calcium levels, increased paper machine runnability and stabilized pH profiles.

## **Improved dewatering**

CO<sub>2</sub> can also be applied to substantially boost dewatering in the paper process. Our patented carbon dioxide applications can be used where increased dewatering or improved water cuts are needed, for example in disc filters, or on the wire section.

## **ACTICO® active control concept**

Using carbon dioxide for pH control has many benefits. The new, environmentally friendly ACTICO® concept from Linde Gas provides total control of pH in the wet end, and eliminates the risk of pH shocks. Through a sophisticated combination of automation and CO<sub>2</sub> injection systems, the ACTICO® concept can be tailored for individual paper machines, according to the specific process parameters that are important in each case.





ADALKA®, GRAFICO®, CODIP®, and ACTICO® are registered trademarks of The Linde Group.  
ACU™ is a trademark of The Linde Group.

# Essential parameters for efficient workflow.

## pH control and pH stability.

By using CO<sub>2</sub> and/or the ADALKA® Process Stabilizer (a combination of CO<sub>2</sub> and NaOH from Linde Gas) together with our pH control systems, pH can be controlled, buffered, and stabilized at an optimum level for every paper process. CO<sub>2</sub> is both more user-friendly and more favorable environmentally than many of the mineral acids it can replace. Its characteristics as a weak acid also have many other chemical benefits in complex chemistry systems like the wet end of a paper machine.

### Eliminating the risk of pH shocks

Where CO<sub>2</sub> or the ADALKA® Process Stabilizer are used to control pH, the concentrations of carbonate and bicarbonate ions (alkalinity or buffer capacity) in the papermaking system waters will be higher than where other acids or bases are used. Adjusting pH with a buffer like ADALKA® gives stable and reliable control over pH and eliminates the risk of pH shocks in the system. Increasing the buffering also means that more acids or bases can be handled in the papermaking system without substantial changes in pH.

pH control and pH stability are essential in modern paper machines, as pH influences most unit operations in one way or another. Experts at many mills believe that maintaining a stable pH is even more important than obtaining a precise pH level, since paper machines are much easier to optimize under stable conditions. Significant improvements and savings can be achieved by optimizing pH.

### Buffer capacity of CO<sub>2</sub>

Dissolved CO<sub>2</sub> creates HCO<sub>3</sub><sup>-</sup> in neutral conditions (pH = 6-10):



HCO<sub>3</sub><sup>-</sup> can neutralize acids and bases.

Acid neutralization:



Base neutralization:



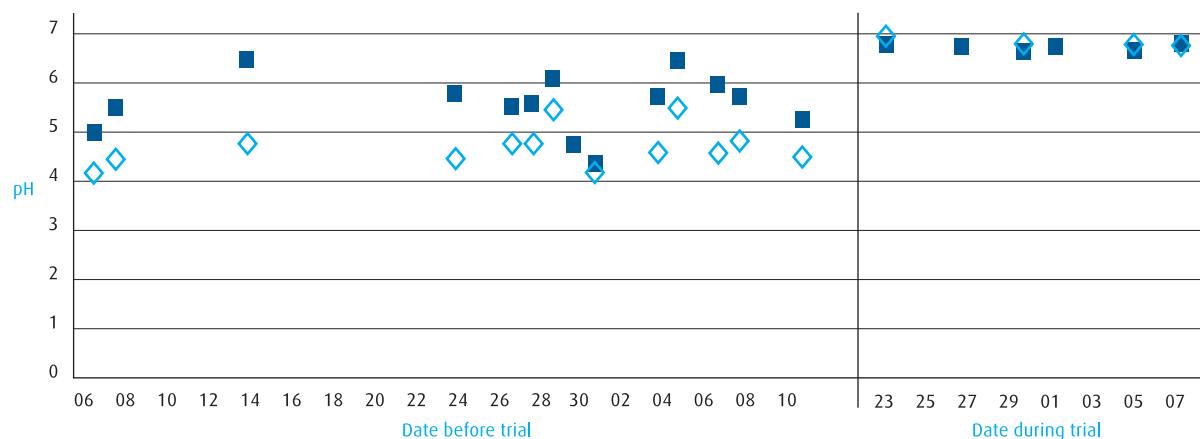
Alkalinity = OH<sup>-</sup> + HCO<sub>3</sub><sup>-</sup> + 2CO<sub>3</sub><sup>2-</sup> - H<sup>+</sup>

### Effects of pH

- Fibers' swelling increases with increased pH.
- Increased pH improves refining, especially of unbleached pulps.
- The dissolution of organic substances from fibers, COD, increases with increased pH.
- Losses in pulp brightness increase at higher pH levels, especially in mechanical pulps.
- The dewatering efficiencies of washing equipment and wire sections decrease with increased pH.
- Precipitation of both organic and inorganic substances is pH-dependent, and sudden changes in pH often lead to precipitation.
- The performances of wet-end chemicals are pH-dependent.

### Stabilizing the pH of the incoming pulp streams in an integrated fine paper mill with ADALKA®

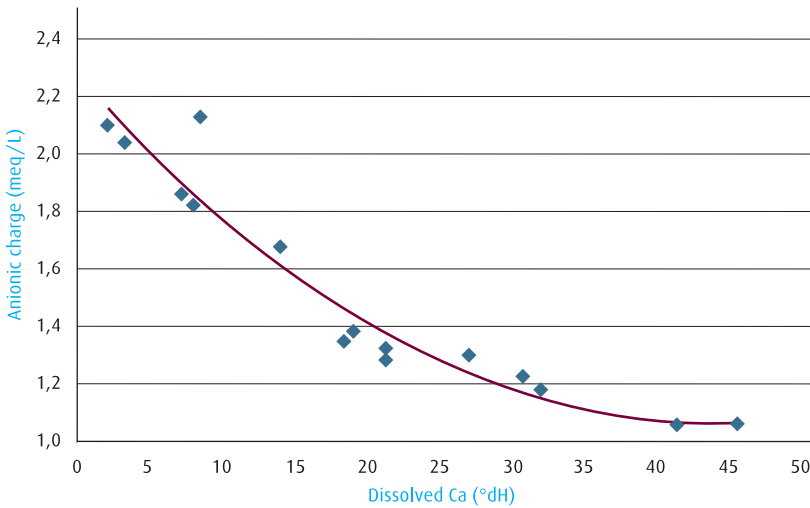
◇ Pine kraft ■ Birch kraft





# Calcium and its effects on papermaking processes.

## The effect of calcium on anionic charge

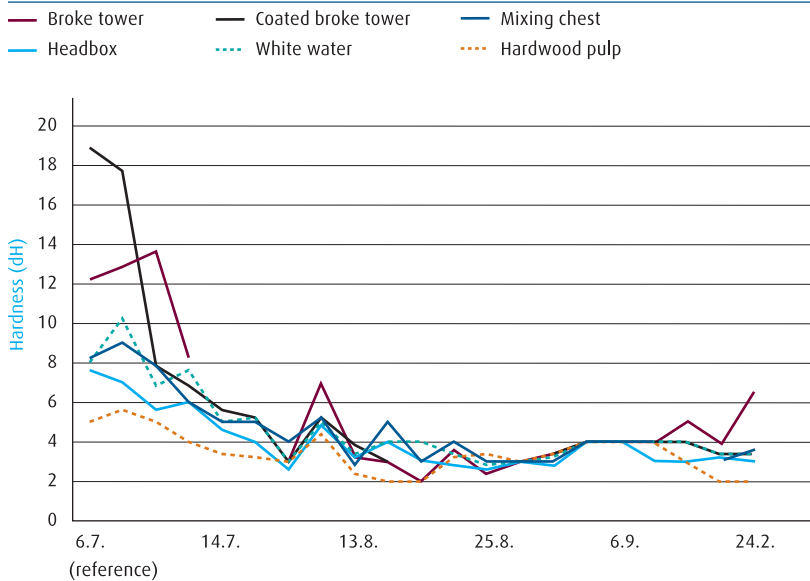


Calcium carbonate ( $\text{CaCO}_3$ ) is present in papermaking systems where recycled fibers, chalk, ground calcium carbonate (GCC), or precipitated calcium carbonate (PCC) are used. The dissolution of  $\text{CaCO}_3$  is extremely pH-dependent. Wherever a strong acid is added, more  $\text{CaCO}_3$  dissolves. This may occur, for instance, in connection with the acidification of de-inked pulp (DIP) or peroxide-bleached mechanical pulp with a strong acid, in the use of naturally acidic mechanical pulps, or where dithionite bleaching residues and microbiological activity occur. Such factors can lead to very high calcium concentrations in the process waters.

### How to minimize $\text{CaCO}_3$ dissolution

It is often difficult to optimize pH in systems that contain  $\text{CaCO}_3$ , which easily can result in an unfavorable pH in parts of the papermaking process. At pH levels higher than 8, only small quantities of  $\text{CaCO}_3$  are dissolved, but running the papermaking processes at such high pH levels often results in other drawbacks, such as poor dewatering and unacceptable brightness loss. With our  $\text{CO}_2$ -based patented solution GRAFICO® Calcium Carbonate Saver, it is possible to have both a low pH and low dissolution of calcium. The addition of "extra" carbonates in the form of  $\text{CO}_2$  and/or ADALKA® ( $\text{CO}_2 + \text{NaOH}$ ) reduces the dissolution of  $\text{CaCO}_3$ , due to the common ion effect, resulting in low concentrations of calcium ions in the process. The best way to avoid problems due to high calcium levels is to minimize the dissolution of  $\text{CaCO}_3$ .

## Through the application of ADALKA® to the coated broke, the calcium levels in the whole mill decreased rapidly



### Effects of calcium

- Research has shown that high concentrations of dissolved calcium and abrupt changes in calcium levels typically coincide with poor production periods:
- The effectiveness of many papermaking chemicals such as starch, retention, sizing and fixatives is decreased with an increased calcium level.
  - Calcium reacts with certain organic materials (anionic trash) to form deposits that can result in spots and holes in the paper product.
  - The anionic charges in papermaking filtrates are a direct function of calcium content. At higher calcium levels, the anionic charge decreases because of reactions with calcium.
  - Calcium also reacts with oxalate, sulfate, and carbonate, producing precipitates that often form persistent, hard deposits in pumps, pipes etc.

# Improve your processes with gas-based solutions.

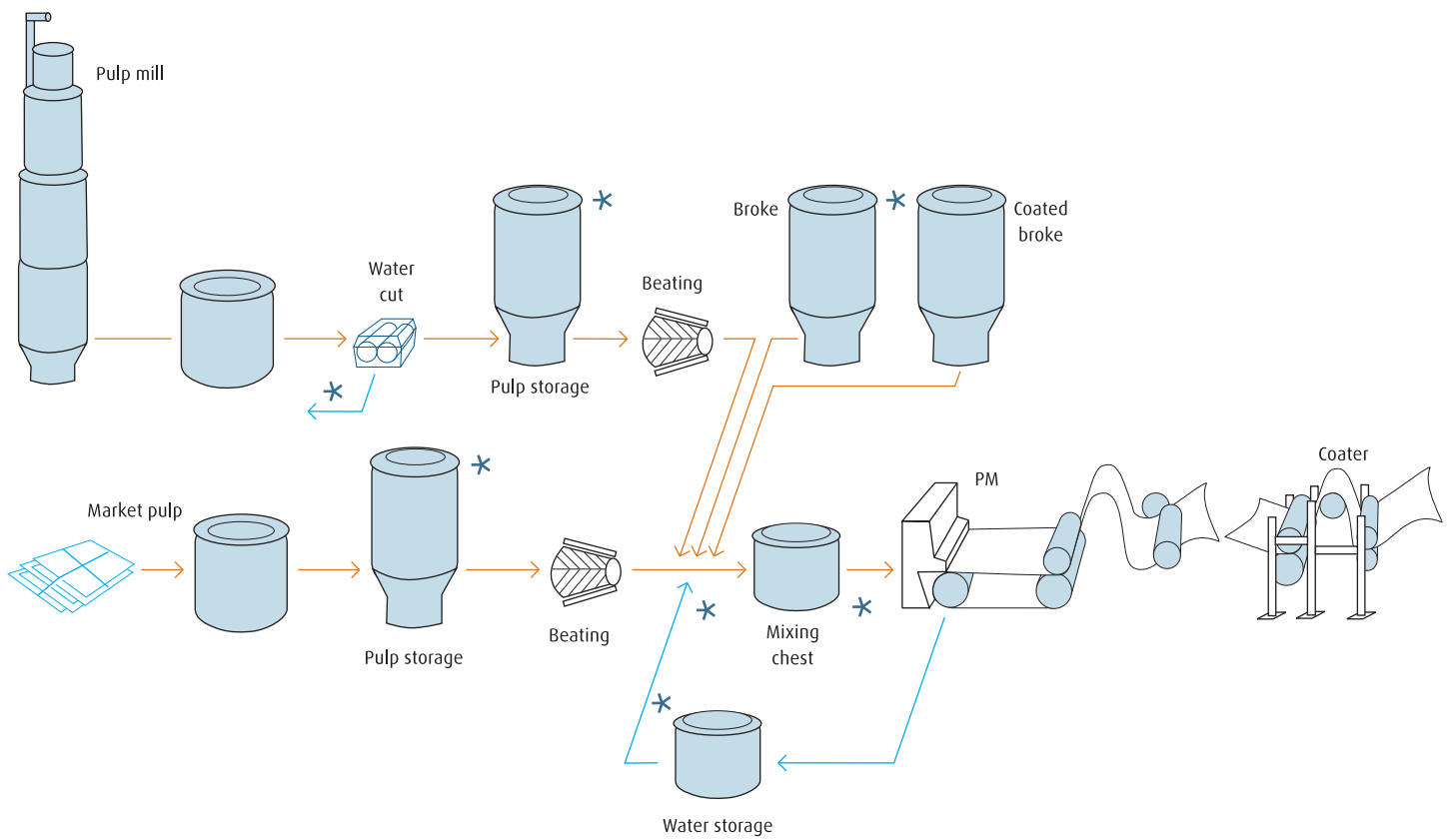
## Gas applications for paper production.

Paper products are often a mixture of different fibers, from chemical and mechanical pulps, including bleached and unbleached pulps, from both market and integrated mill sources. Different chemicals, fillers, and coatings are successively added during the papermaking process and then partly returned to the process through the addition of broke and coated broke. To control pH, optimize pH profile, and increase pH stability, the ADALKA® Process Stabilizer can be used. Addition points are usually early in the stock preparation or in the broke system. Using ADALKA® also minimizes the dissolution of the calcium carbonate ( $\text{CaCO}_3$ ) from the filler or coating by increasing the amounts of bicarbonates and carbonates present. Carbon dioxide ( $\text{CO}_2$ ) can be added later in the process to optimize pH in the short circulation and wire sections, irrespective of the pH earlier in the process.

### Advantages of gas-based solutions for papermaking processes

- Through the use of the ADALKA® Process Stabilizer before refining, a stable and controlled pH can be obtained. That gives stable refining with even strength properties.
- The incoming pulp streams can be stabilized and pH variations minimized through the use of ADALKA®.
- Broke may be stabilized with ADALKA® or  $\text{CO}_2$ . With  $\text{CO}_2$ , pH can be kept low enough to avoid brightness loss, which is particularly important in coated broke. With ADALKA®, pH can be stabilized at a level high enough to avoid the dissolution of  $\text{CaCO}_3$  due to bacteria.
- Calcium carbonate dissolution is avoided by using ADALKA® in the papermaking process, leading to low calcium levels.
- Bicarbonate ions catalyze and give better AKD (alkyl ketene dimer) sizing. The bicarbonate ions can be obtained through ADALKA®.
- Calcium sulfate in the coating gives high calcium levels into the processes, which makes a stable pH important for runnability. The stable pH and buffered system can be achieved with ADALKA®.
- By using the ACTICO® active control concept, the pH, for example in the short circulation and the stock preparation, can be adjusted separately.
- Using ADALKA® or adding  $\text{CO}_2$  minimizes calcium levels in papermaking processes using  $\text{CaCO}_3$ , reducing precipitation and improving the functioning of chemicals.
- Unwanted changes in pH are minimized with a buffered system. For higher buffering, ADALKA® is recommended, but  $\text{CO}_2$  also serves to buffer systems.

Paper production



\* Possible addition points for gas-based applications from Linde Gas

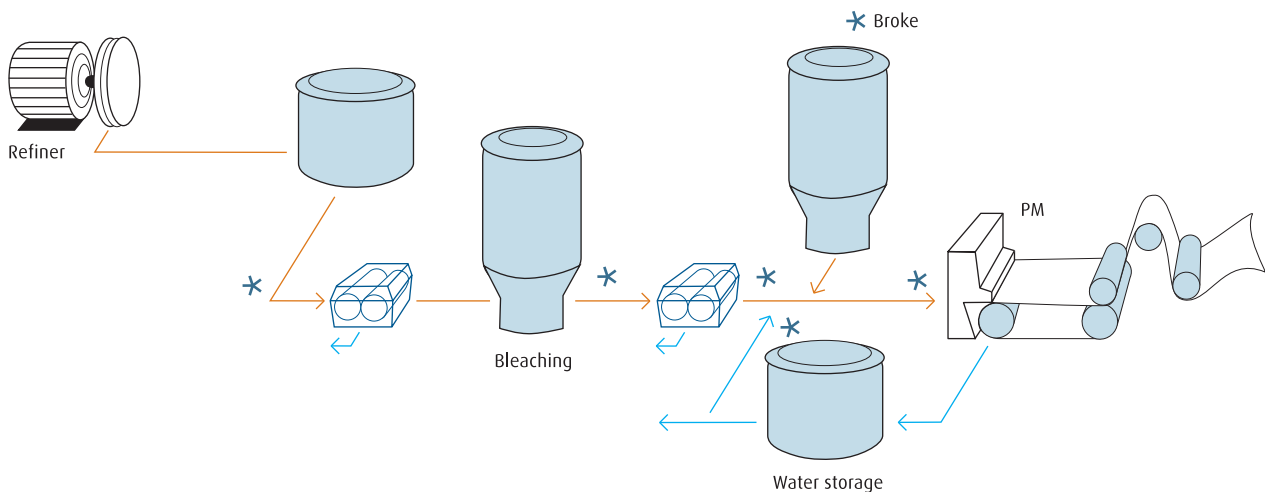
# Fact, not fiction: our gas applications can improve your products. Mechanical pulp.

Paper can be produced from mechanical pulp in either slightly alkaline, neutral, or acidic conditions. The benefits of using CO<sub>2</sub>-based applications are greatest in slightly alkaline and neutral papermaking conditions. The process always becomes neutral if calcium carbonate (CaCO<sub>3</sub>) is used as a filler. In neutral papermaking, the higher pH levels can lead to increased dissolution of organic material (COD) and brightness loss compared to acidic papermaking.

## Effective process improvement with CO<sub>2</sub>-based solutions

In the GRAFICO® method from Linde Gas, CO<sub>2</sub> is used to lower pH levels without significant dissolution of CaCO<sub>3</sub>. The GRAFICO® Calcium Carbonate Saver minimizes brightness loss, improves dewatering, and favorably decreases the amounts of dissolved material. Depending on the process conditions, suitable addition points may be in the short circulation, process waters, or pulp streams. The washing stage after peroxide bleaching can also be improved by using CO<sub>2</sub>. After peroxide bleaching, the pulp needs to be acidified. Here, both CO<sub>2</sub> additions and the ADALKA® Process Stabilizer are interesting options to use, eventually in combination with other chemicals. The benefits of such applications include low calcium levels and low brightness loss. In papermaking systems with large amounts of acidic mechanical pulp, added dithionite, microbiological activity, or poly-aluminum chloride (PAC) etc., pH levels are often low in parts of the system. This can result in sudden pH changes during different stages of the process, leading in turn to precipitations and high calcium levels. To avoid this, such systems can be buffered by using ADALKA® at a suitable addition point, for example into the broke or the clear filtrate. In this way the whole system is buffered with bicarbonate ions, giving both a stable pH and low calcium levels. In acidic papermaking conditions, using the ADALKA® Process Stabilizer to buffer certain process waters can be advantageous to off-set microbiological activity and dithionite acidity.

## Mechanical pulp



\* Possible addition points for gas-based applications from Linde Gas



# De-inked pulp (DIP).

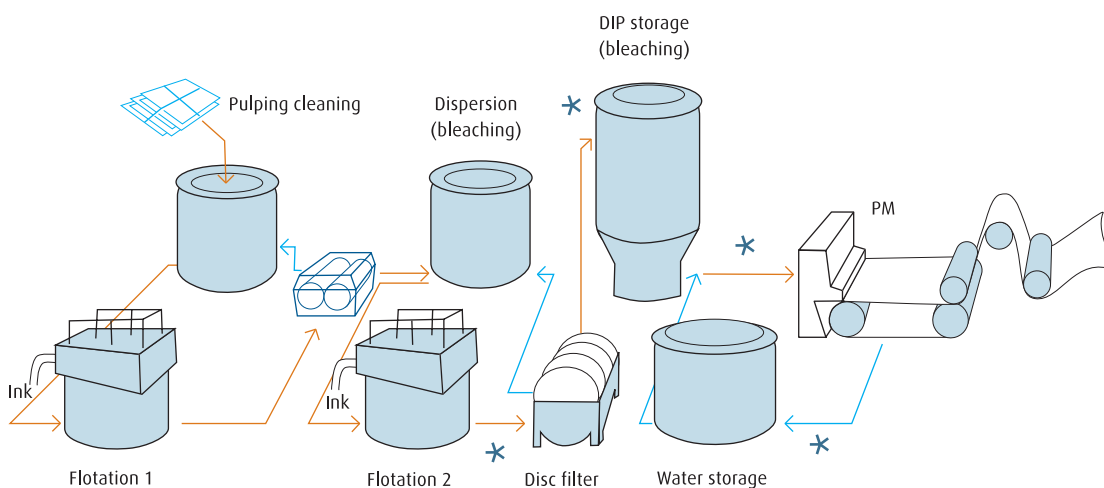
The patented application CODIP® Process Improver has been developed primarily for newsprint production, where DIP is the main raw material and carbon dioxide is added to the papermaking process to obtain an optimized pH profile. To achieve the best possible results, two CO<sub>2</sub> addition points are often used, with one in the DIP plant and one later in the process, around a storage tower or in the short circulation. Acidification with CO<sub>2</sub> instead of H<sub>2</sub>SO<sub>4</sub> or SO<sub>2</sub> results in lower calcium levels.

In some papermaking systems containing DIP or combinations of DIP and mechanical pulps, the pH in the overall system can be low, due to such factors as microbiological activity or large dithionite dosages. This low pH results in high calcium levels due to the dissolution of CaCO<sub>3</sub>, which in turn can lead to problems with starch performance, for example. In these cases, the ADALKA® Process Stabilizer can be used to reduce calcium concentrations.

## Advantages of Linde Gas applications used in various DIP mills

- Improved washer capacity and better water cut between the DIP plant and the paper machine.
- Improved flotation of DIP through controlled calcium levels in the DIP plant.
- Fewer spots and holes in the paper, and reduced deposits in the wire and press sections, through lower calcium levels in the process and optimized pH profiles.
- Reductions in calcium levels of up to 75% in paper machine filtrates compared at the same pH.
- Easier filler usage through minimized dissolution of CaCO<sub>3</sub>.
- Minimized brightness loss and dissolution of organic material.
- No difficult summertime periods.
- No calcium oxalate scaling.
- Lower levels of sulfate ions in effluent and sludge.

## De-inked pulp (DIP)



\* Possible addition points for gas-based applications from Linde Gas



## Gas and equipment.

The gas carbon dioxide (CO<sub>2</sub>) is a very important part of natural cycles. CO<sub>2</sub> is exhaled by humans and other animals, and consumed by plants using natural processes that release oxygen back into the atmosphere. Carbon dioxide is normally produced as a by-product from other chemical processes. Using CO<sub>2</sub> produced in such ways is environmentally friendly and does not contribute to the greenhouse effect.

Carbon dioxide is delivered and stored as a liquid, to save on space and transportation costs. Linde Gas provides the customer with all the tanks and equipment needed to handle and evaporate CO<sub>2</sub> safely and economically. Many of our tanks are remotely monitored from Linde Gas, so that we can guarantee supplies more effectively, minimize transportation and improve safety.

### CO<sub>2</sub> dissolution

Carbon dioxide is a gas with relatively high solubility in water. Pressure turbulence, pulp concentration, retention time, and pH are key parameters when choosing the right method and position for injecting gas into pulp and papermaking processes. When the injection system for carbon dioxide is properly designed, the use of gas does not cause any problems with foaming or de-aeration.

### ACU™ alkalinity control unit

In some of our applications, CO<sub>2</sub> is added to the process in the form of a bicarbonate/carbonate solution. To be able to supply the buffering solution at any pH (typically in the range of pH 7.2–10), Linde Gas has developed the ACU™ alkalinity control unit. This fully automated reactor produces bicarbonate/carbonate in a water solution that can easily be added to processes. The advantages of using our ACU™ system, compared to the traditional use of sodium bicarbonate as a powder, are clear. Alkalinity and pH can be controlled independently of each other, the system is fully automated and requires no manual labor, and it's a cost-efficient solution.



# Reference customers.

Linde Gas has installations at various stages between the start of the stock preparation and the headbox in around 40 paper machines in Europe and North America. Leading paper producers in these regions use CO<sub>2</sub>-based solutions from Linde Gas. At different addition points, these innovative gas applications can, for example, control pH and buffer calcium levels, enabling our customers to run their high-capacity paper machines at optimum speed and efficiency.

## Using a broad range of applications: Kruger Wayagamack

Kruger is a privately owned company that today is one of the leading producers of magazine paper in North America. At Kruger Wayagamack, a new LWC paper machine with online coating, PM4, was started in November 2003. The capacity is 220,000 tons a year, and the design speed is 1,500 m/min. The mill is located in Trois Rivières, Quebec, Canada.

PM4 at Kruger Wayagamack is one example of a paper machine that uses CO<sub>2</sub>-based applications from Linde Gas. The paper machine runs under neutral conditions and uses calcium carbonate in the coating. A combination of the ADALKA® Process Stabilizer, the ACU™ alkalinity control unit, and CO<sub>2</sub> has been used since the startup. Kruger Wayagamack uses these gas applications as innovative and efficient tools to control PM4's pH, buffer capacity, and calcium levels from the start of the stock preparation to the short circulation, using several different addition points.

## More examples of our references are:

- Assi Domän Frövi, Sweden
- M-real Kangas, Finland
- Stora Enso Anjalankoski, Finland
- Peterson Linerboard, Norway
- UPM Nordland Papier, Germany
- SCA Laakirchen, Austria
- UPM Chapelle Darblay, France

The Kruger Wayagamack paper mill in Trois Rivières, Quebec, Canada.



# Getting ahead through innovation.

With its innovative concepts, Linde Gas is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

Linde Gas offers more. We create added value, clearly discernible competitive advantages and greater profitability. Each concept is tailored specifically to meet our customers' requirements – offering standardized as well as customized solutions. This applies to all industries and all companies regardless of their size.

If you want to keep pace with tomorrow's competition, you need a partner by your side for whom top quality, process optimization and enhanced productivity are part of daily business. However, we define partnership not merely as being there for you but being with you. After all, joint activities form the core of commercial success.

**Linde Gas – ideas become solutions.**

